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X-ray $L_{2,3}$ resonant Raman scattering from NiO: Spin flip and intermediate-state relaxation

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We present measurements of x-ray resonant Raman scattering from NiO with $L_{2,3}$ excitation and calculations in an ionic model based on the process $(2p^63s^23d^8)\rightarrow(2p^53s^23d^9)\rightarrow(2p^63s^13d^9)$. The agreement between theory and experiment is good from below threshold up to 2.5–3 eV above threshold. By comparing theory and experiment, we show the effect of crystal-field splitting and the contribution bringing the Ni^{2+} triplet ground state to a singlet final state with excitation above the L_3 edge. When the excitation energy exceeds the L_3 threshold by about 3 eV, we present evidence that the intermediate state in the scattering can also relax to a state similar to that created with threshold excitation. We suggest d-d excitation and electron-hole pair excitation as the origin of this relaxation. [S0163-1829(97)50624-2]

In x-ray electronic resonant Raman scattering (RRS) a resonant excitation at threshold creates an intermediate state with a deep core hole which decays via an inner-shell transition, i.e., with the emission of a photon having much lower energy than the incoming photon. Hereafter a RRS spectrum is defined as the scattered intensity vs the outgoing photon energy ($h\nu_{\rm out}$) keeping the incoming photon energy ($h\nu_{\rm in}$) constant. In systems which can adequately be described by some average field approximation, the variation of the energy of the electron added to the valence states due to excitation with different photon energies has little effect on the inner-shell transition, so that the Raman spectrum is basically independent of ($h\nu_{\rm in}$). In particular, in a bandlike system the spectrum is strictly independent of the excitation energy.[1] On the other hand, if many-body multiplet effects are important, as in atomiclike cases, the RRS spectra depend strongly on ($h\nu_{\rm in}$) as shown by rare-earth systems across the L edges.[1–3]

It is thus also interesting to apply RRS to strongly correlated systems containing *late* $3d$ transition metals (TM's) which in general cannot be described by a standard bandlike model and, needless to say, are extremely important materials (e.g., high-T_c superconductors). In this connection the more appealing case is $L_{2,3}$ excitation giving a direct dipole transition to the $3d$ states. However, this work has been discouraged up to now by the large lifetime broadening, since it is not *a priori* evident that the results are meaningful. In fact in late transition-metal $L_{2,3}$ RRS the dipole-allowed final states have a $3s$ hole contributing about 3 eV to the broadening. This broadening decreases considerably along the $3d$ series on going to lower atomic numbers. In this case the research is more feasible so that, to the authors' knowledge, the only published work deals with Ca-$L_{2,3}$ RRS in CaF_2 investigated experimentally in pioneering work by Rubensson *et al.*[4] and discussed by de Groot with atomiclike calculations[5] (the related K-halide problem is addressed in Ref. 6). The present study deals with RRS in a strongly correlated system containing a late $3d$ TM, i.e., NiO. This is one of the most natural candidates due to its well-known importance,[7] and due to the fact that the Ni configuration is basically d^8, so that it has a simple RRS final state $(2p^63s^13d^9)$ containing only two holes. The present work is based on a comparison between the measurements and ionic calculations of the spectra expected from Ni^{2+} in the process $(2p^63s^23d^8)\rightarrow(2p^53s^23d^9)\rightarrow(2p^63s^13d^9)$, without any rearrangement in the intermediate state. We show that the main calculated features are seen in spite of the final-state lifetime broadening, demonstrating that RRS is a useful approach in this field. In particular we show in a direct way that Ni^{2+}, which is triplet in the ground state, can flip to a singlet final state. Moreover, the experiment adds important information since we give evidence of an extra contribution appearing in RRS spectra when the excitation is several eV above threshold. We show that a reasonable origin of this component is the relaxation of the intermediate state, i.e., a modification of the intermediate state before radiative decay due to a solid state effect likely to be the (d-d) excitations, and to the excitation of electron-hole pairs across the gap. This is an important piece of experimental information which can stimulate further research on intermediate-state modification, which is emerging as a crucial issue in resonant soft-x-ray scattering.[8–12] For all these reasons the present results have an interest well beyond the specific NiO case.

The measurements were made at the undulator based BL26/ID12B of the European Synchrotron Radiation Facility;[13] the scattered light was analyzed with a grating spectrograph, allowing parallel acquisition in a 40-eV energy interval,[14] and matched to the exit slit of the beamline monochromator with refocusing optics. The x-ray-absorption spectra (XAS) are obtained in the same apparatus from the sample drain current. The RRS spectra have been taken at selected ($h\nu_{\rm in}$) shown by the arrows in Fig. 1(A), where the horizontal bars indicate the bandpass which is typically 1.6 eV (at 860 eV we used 4.1 eV for intensity reasons). In general a typical counting rate was three counts per second integrated over the whole spectrum having chosen a $\cong$1.2-eV linewidth in the analyzer. In Fig. 1(A) the XAS spectra with 0.3-eV bandpass is given. The sample was a single crystal cleaved in air, and the photon incidence was 30°. Every 2 h the spectrum at threshold (No. 3) was measured to test the stability of the whole system.

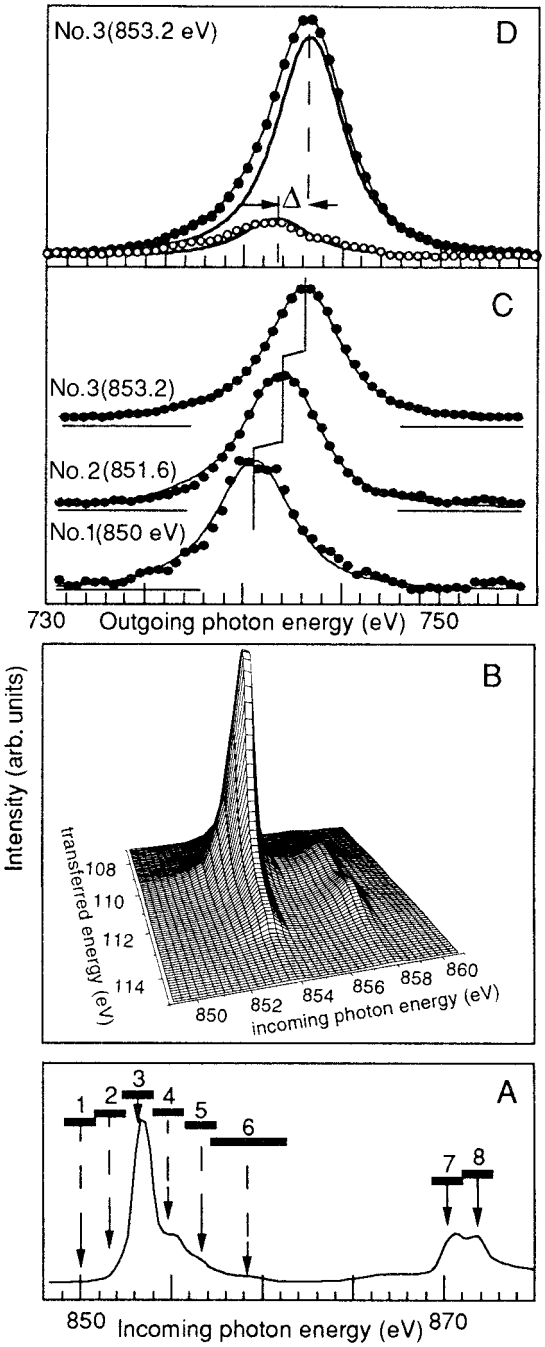

FIG. 1. (A) $L_{2,3}$ absorption spectrum of NiO. The arrows and the horizontal bars indicate the excitation energies and the bandpass in RRS, respectively. (B) A three-dimensional plot of the calculated L_3-RRS cross section as a function of the incoming and of the transferred energy. (C) RRS spectra excited below and at the L_3 threshold; the solid lines are the theoretical simulation including bandpass and resolution effects. (D) Decomposition (as explained in the text) of the spectrum at threshold to emphasize the crystal-field effect shown by the separation Δ.

The RRS was calculated with the second-order formula in the ionic limit

$$I(h\nu_{\rm in},h\nu_{\rm out}) \propto \sum_f \left| \sum_n \frac{\langle f|D^{(1)}|n\rangle\langle n|D^{(1)}|g\rangle}{h\nu_{\rm in}+E_g-E_n+i\Gamma_n/2} \right|^2 \times \delta[(h\nu_{\rm in}-h\nu_{\rm out})-(E_f-E_g)] \qquad (1)$$

using Cowan's program.[15] The labels g, n, and f indicate ground, intermediate, and final states. The Lorentzian widths are taken from Ref. 16. The values for the Coulomb interaction were scaled down to 80% to simulate the effect of the solid. An octahedral crystal field $10Dq$ equal to 1.5 eV has been applied. The configurations are $|3d^8\rangle$, $|2p3d^9\rangle$, and $|3\underline{s}3d^9\rangle$ for the ground, intermediate, and final states, respectively (underline means a hole). One can distinguish four distinct final states. For zero $3d$ spin-orbit splitting coupling these are $|(3\underline{s}\,\underline{e}_g)^{1,3}E_g\rangle$ and $|(3\underline{s}\,\underline{t}_{2g})^{1,3}T_{2g}\rangle$. The singlet-triplet splitting is $(2/5)G_{\rm sd}=4.1$ eV. The other numerical parameters are taken from Ref. 17. The spectral weight of these features strongly depends on the intermediate state which is excited by the incoming photons having different energies. An overview of the evolution of the spectral function is seen at the L_3 edge from the three-dimensional plot of Fig. 1(B), also including the effect of the final-state lifetime; the cross section is given as a function of the incoming photon energy ($h\nu_{\rm in}$) and of the transferred energy ($h\nu_{\rm in}-h\nu_{\rm out}$), which are the natural coordinates given by formula (1). This is the cross section in an experiment with infinite resolution, and the RRS spectra in this case are the sections at constant incoming photon energy.

As a guideline to the following discussion it is useful to give a qualitative explanation of the ($h\nu_{\rm in}$) dependence of the theoretical RRS spectra. Obviously triplet states have on the average a lower energy than singlet states. Even in the presence of strong $2p$ spin-orbit interaction, we find that states at the low-energy side of a spin-orbit-split manifold have more triplet character than those on the high-energy side. Since the Ni^{2+} ground state is a triplet $|(\underline{e}_g^2)^3A_2\rangle$, and dipole transitions conserve spin, one would generally expect the triplet final states to have more spectral weight. This is certainly the case at the threshold where the intermediate state has a strong triplet character. Since the ground state does not contain t_{2g} holes, the structure due to the crystal-field splitting obtains much less weight, and gives rise only to a small line-shape asymmetry at threshold. When we go to higher energies (typically 3 eV above threshold) the states have more singlet character, and transitions from triplet ground state into a singlet final state become possible. Thus the cross section has two peaks [see the three-dimensional plot of Fig. 1(B)] having singlet and triplet characters, each of them containing, within the lifetime broadening, e_g and t_{2g} contributions.

In order to compare the theory and the experiments one has to keep in mind the following points:

(i) In soft-x-ray inelastic scattering, the modification of the spectral shape due to self-absorption is very often a problem. An advantage of RRS is that the emitted photons are only weakly absorbed, and without deformation of the spectrum, since the absorption well below the resonance is small and basically constant. On the other hand, the large absorption in the excitation channel gives rise to strong saturation effects. Since most of the relevant information is given by the spectral shape, there is no point in correcting for saturation, and we do not discuss the relative amplitudes of the spectra.

(ii) The excitation bandpass and the resolution in the analysis of the scattered light must be included in the theory to simulate the experiment, although these effects are less

important than final-state lifetime which is the dominant contribution to the broadening. In the simulation one has to take into account that the spectra are measured as a function of the outgoing photon energy, and not of the transferred energy.

The experimental results up to the L_3 threshold are given in Fig. 1(C) (black dots). The peak position changes linearly with $h\nu_{\text{in}}$ (i.e., constant transferred energy) as expected in the RRS regime below threshold, and the line shape is dominated by the Lorentzian final-state broadening Γ_f. The solid lines are the theoretical simulation including bandpass and resolution effects, in addition to the lifetime broadening (an excellent agreement is found with $\Gamma_f = 3.2$ eV, a value consistent with Ref. 16). The line shape is not symmetric, as is better seen in Fig. 1(D) (black dots) showing spectrum No. 3 (at 853.2 eV). As discussed above, the theory shows that the lower-photon-energy side (higher transferred energies) of the peak is slightly affected by crystal-field effects, while the other side is not. This helps in the decomposition of the measured peak. One can define an approximate peak shape by taking a symmetric peak having the same shape as the high-energy side of the measured peak. With this line shape the best fit to the measured curve is obtained with two components given by the heavy lines in Fig. 1(D), showing also that the residues are very small since the difference spectrum (open dots) between the measurements and the major component is very close to the other component. This decomposition is in excellent agreement with the theory, showing in a direct way the effect of the octahedral crystal-field splitting $10Dq$. Thus RRS gives very detailed information about the threshold excitation not directly accessible to measurements integrated along $(h\nu_{\text{out}})$.

The evolution above the L_3 threshold is shown in Fig. 2(A) comparing measured spectra No. 3 and No. 4 separated by 1.7 eV along $(h\nu_{\text{in}})$. A deformation at higher $(h\nu_{\text{out}})$ is seen in spectrum No. 4 with respect to No. 3, with a very clear counterpart in the theory. At the L_2 threshold the theory predicts the spectra given in Fig. 2(B), and having two features due to the singlet and triplet final states of the two final holes (singlet at higher transferred energies, i.e., at lower $h\nu_{\text{out}}$). The spectral shape is in good general agreement between theory and experiment, and in particular we see in both spectra the singlet features shown by the arrows. The statistics and the lifetime broadening prevent an accurate assessment of the experimental separation between singlet and triplet. With these precautions in mind one can say that the experimental separation is consistent with theory in spectrum No. 7, and slightly smaller in spectrum No. 8, so that the theoretical value of 4.1 eV is not inconsistent with the results. In conclusion a simple description based on formula (1) is fairly satisfactory from below each threshold up to an energy 2.5–3 eV above threshold (this estimate also includes the excitation bandpass).

We next consider the excitation between the L_3 and the L_2 threshold. In this case the theory suggests that the singlet to triplet separation should be observed, as shown by the theoretical simulation given in the upper part of each panel (thin solid lines) of Fig. 3(A) (case No. 5) and Fig. 3(B) (case No. 6). In fact the experimental results (black dots in Fig. 3) are considerably different with respect to the theory. In both panels the dashed line is the spectrum at threshold

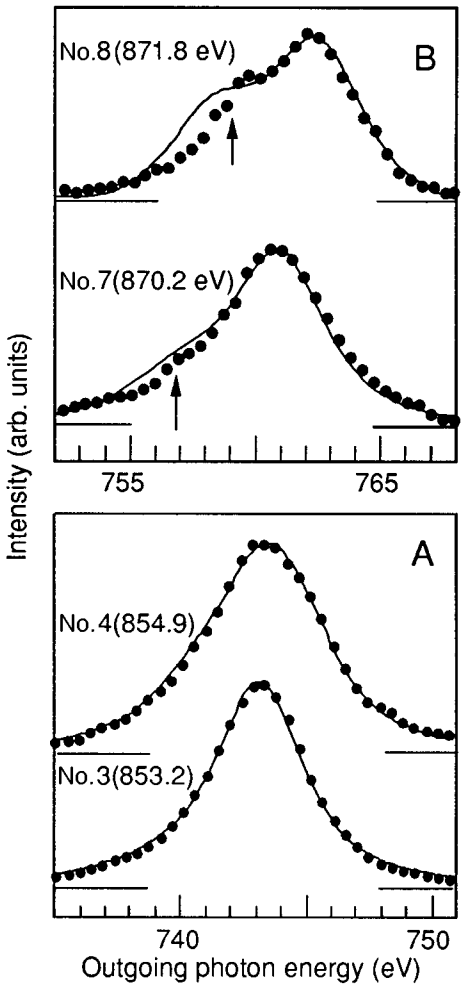

FIG. 2. (A) The RRS spectra (black dots) excited at the L_3 threshold (No. 3) and excited at 1.7 eV above threshold (No. 4) normalized to the same height to show the shape modification. The theoretical simulations are given by the thin lines superimposed to the experimental points. (B) RRS spectra (black dots) with excitation in the L_2 region (No. 7 and No. 8) compared with the theoretical simulations (thin lines superimposed on the experimental points).

(No. 3) given with an amplitude discussed below. The width of the spectra is much larger in cases No. 5 and No. 6 (black dots) than at threshold (dashed curve). This is consistent with the spectral intensity being added in regions where singlet and triplet contributions are expected, and this is direct evidence of the spin-flip transitions from the triplet ground state to the singlet final state. The presence of singlet-triplet contributions in the final state is analogous to the situation seen in Ca^{2+} (Ref. 4), but Ca is somewhat less interesting since it is d^0 in the initial state, whereas here we have a triplet ground state. An important empirical result is that an appropriate subtraction of the spectrum at threshold from the measured spectra generates a difference spectra (open points) in agreement with the theory within the accuracy allowed by lifetime broadening and bandpass. The best weight of the spectrum to be subtracted is that given by the dashed lines, and is chosen to have the best agreement between the difference spectrum and the theory. This suggests that the spectra excited well above threshold can be described approximately as a superposition of two contributions coming from channels in competition.

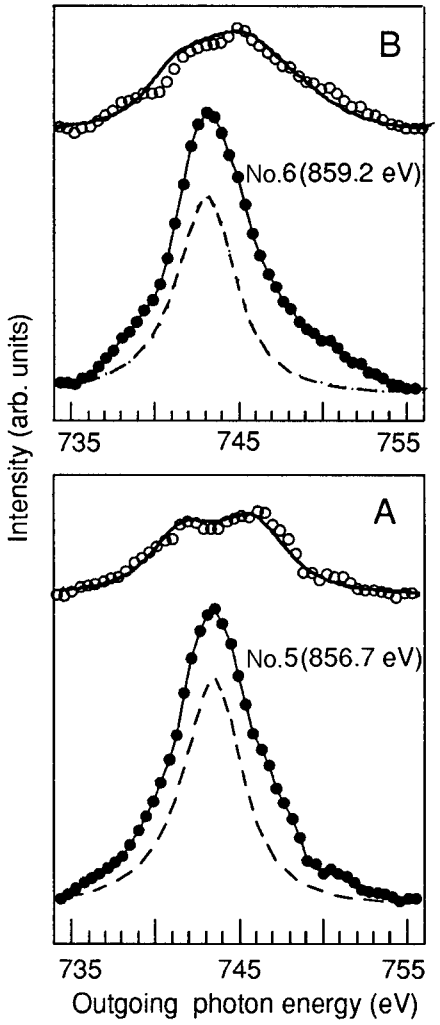

FIG. 3. (A) The RRS excited at 856.7 eV, given by the black dots, and the theoretical simulation in the upper part of the same panel (thick continuous line). The measured spectrum is compared with the spectrum at threshold (dashed line). The open dots give the difference between the two spectra; the amplitude of the spectrum at threshold is chosen to give the best agreement between the difference spectrum and the theoretical simulation. (B) The same as in panel (A), with an incoming photon energy of 859.2 eV.

(i) One coming from the Raman scattering as calculated above, i.e., without rearrangement in the intermediate state (hereafter referred to as unrelaxed component).

(ii) Another coming basically from the same d^9 multiplet obtained with threshold excitation, although the incoming photons excite to d^9 terms much higher in energy. This implies a transformation of the intermediate excited state to the lower-lying states due to the interaction with the solid (this contribution will be referred to as the relaxed component). Note that the relaxed contribution cannot be the characteristic fluorescence coming from the $(2p^5 3s^2 3d^8) \rightarrow (2p^6 3s^1 3d^8)$ decay since, in the presence of the core hole, the threshold to the continuum is around 866 eV [see the small shoulder in XAS of Fig. 1(A) and Ref. 18].

These results are strong evidence that the rearrangement in the intermediate state is very important when the excitation is several eV above threshold. Since this process does not take place at small energies above threshold, it is reasonable to attribute the relaxation to processes having some threshold such as the $(d$-$d)$ excitations in the gap and the electron-hole pair excitation across the gap [note the connection with the $(d$-$d)$ excitations in MnO seen in x-ray resonant inelastic scattering[19]]. This would give a threshold consistent with the present energy scale. Needless to say, a complete assessment of this problem needs further work[20] with other experimental methods and in a variety of TM oxides. One of the goals of the present paper is also to stimulate these important researches, which have the chance to give additional insight into the dynamic aspects of these systems.

In conclusion, we have shown that x-ray RRS across the $L_{2,3}$ thresholds in NiO gives relevant information in spite of the considerable final-state lifetime broadening. We have observed the effect of the crystal-field splitting, the separation of singlet and triplet final states, and in particular spin-flip processes. Moreover, when the excitation is 2.5–3 eV above the L_3 threshold, the experimental results show a component not present in an ionic theory calculated without rearrangement in the intermediate state. Within the accuracy allowed by the lifetime broadening, this component has the same shape as the spectrum obtained with excitation at threshold. For this reason this component is attributed to the relaxation of the intermediate excited state via threshold mechanisms such as $(d$-$d)$ excitations and electron-hole-pair excitation across the gap.

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